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Use of the Biochar Obtained by Slow Pyrolysis from *Ulex Europaeus* in the Removal of Total Chromium from the Bogotá-Colombia River Water

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This paper explores the use of biochar obtained from the pyrolysis of *Ulex Europaeus*, an invasive species in the mountain ecosystems of Colombia, for the removal of total chromium from the water. The investigation was developed in two phases. First, the slow pyrolysis of *Ulex Europaeus* was carried out at varying temperatures (450, 550, and 650° C) to produce a biochar that was characterized by texture, surface area, and percent yield. In the second phase, the biochar then was used to test the removal of chromium from natural water samples collected from the Upper Bogotá River Basin. The removal of chromium with a commercial activated carbon also was assessed as a control. Finally, measurements of total chromium collected were used to evaluate biochar removal efficiencies. The biochar produced at both 550° C and 650° C was found to remove over two times the amount of chromium compared the activated carbon, demonstrating that biochar from *Ulex Europaeus* is an effective sorbent for total chromium.

1. Introduction

Ulex Europaeus is original from the Atlantic and Mediterranean of Western Europe and included in the list of the 100 highly aggressive invasive species in the world (Díaz, 2009, as cited in Cárdenas et al., 2017). This species reproduces vegetatively through adventitious root and stem shoots and sexually through seeds, with seed dispersal being the main reproductive strategy. (Aguilar, 2010).

This plant represents a distinct threat to native Colombian ecosystems, mainly the Andean, high Andean Forest, paramo, and mountain wetlands. In these ecosystems, it causes a loss of biodiversity by displacing the native flora and altering soil conditions due to nitrogen fixation and soil acidification (Corporación Autónoma Regional, 2015). A possible solution for this problem is eradication through the cutting of the species, and subsequent burning in authorized ovens of large volumes of plant material.

The Biochar is a positive alternative for the use of organic waste, which would otherwise be disposed of. Traditionally, biochar has been applied as soil amendment but can also be used in the process of removal and adsorption of pollutants in water. Its efficiency as a sorbent depends on surface area and porosity. Other features of its efficiency include percent yield, moisture content, and the conditions of the production process (Del Amo Mateos, 2018).

To obtain the biochar a slow pyrolysis process is carried out, which refers to the partial combustion of the biomass by uniform and slow heating approximately 0.01-2 ° C / s at temperatures between 450 and 650 ° C, in the absence of oxygen, where the gases produced are captured to obtain syngas or synthesis gas, obtaining approximately 40% of the original biomass in biochar (Hernández and Piñeros 2017).

Based on the above, the use of biochar is proposed to remove total chromium from water, using samples from the Upper Bogotá River Basin, this region is known for its chromium contamination problem derived from discharges of wastewater from the tannery industry, which contributes between 30 and 40% of the total chromium to its waters (Belay, 2010), In July 2014, average concentrations of chromium were found to be 0.521 mg/L in the section of the river that crosses the municipality of Chocontá (Castañeda and Florian, 2019).

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In some parts, these waters are used in irrigation systems and can infiltrate directly into the soil and be absorbed by plants. One study found high concentrations of chromium in soils for growing Peas and Broad beans at Hacienda Casablanca in the municipality of Chocontá, which is located on the banks of the Bogotá River and uses its waters to irrigate crops (Camacho and Robles, 2009).
Another consequence of the chromium contamination is in the aquatic biota beecause high concentrations of chromium can damage the gills of fish that swim near the discharge point, in addition, chromium can cause respiratory problems, birth defects, infertility and tumor formation in animals (Zarate, 2007), moreover Avenant-Oldewage and Marx (2000) found that some species of fish can accumulate up to 100 times the concentration of chromium present in water, which allows the contaminant to enter the food chain.

2. Sample collection

2.1. Collection site of the Ulex europaeus plant

The area considered for this study is set on the located to the east of the city of Bogotá, on the eastern mountain range of the Colombian Andes (Ocampo 2019). This region offers ecosystem benefits and services among which are the water supply with about 1,120 basins that become water corridors and supply the high biodiversity of flora and fauna (Veeduría Distrital, 2018). With 13,224 ha of its territory, they make up the Protective Forest Reserve Bosque Oriental de Bogotá (Secretaría Distrital de Planeación, sf) where only 64% are native species (Ocampo, 2019). In 2010, the Protective Forest Reserve Bosque Oriental de Bogotá had only 57 ha entirely covered by thorny broom (Corporación Autónnoma Regional, 2010). In Bogotá-Colombia, *Ulex europaeus* has invaded more than 3,000 ha, occupying peri-urban and rural areas. (Garavito, 2010). Figure 1 shows the area where the samples of *Ulex Europaeus* were collected. In this area, the vegetation of the low Andean forest predominates, and the San Francisco stream passes 300 m away with no sites of discharge of pollutants to the soil and water identified.

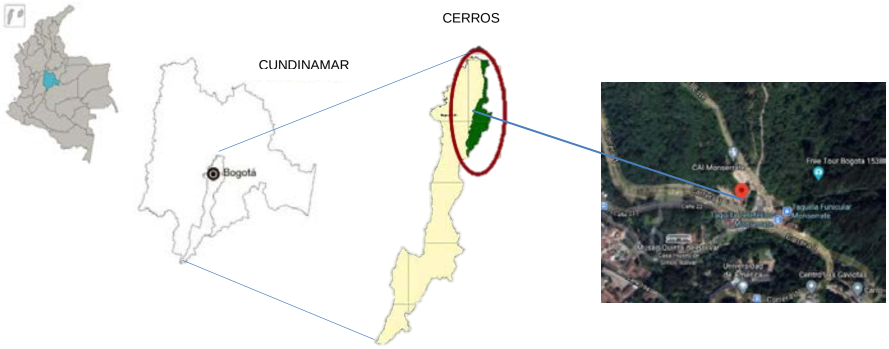

Figure 1: Ulex europaeus sample collection site.

2.2. Collection site of the water sample.

The study area is in the Río Alto Bogotá Sub-basin, in the province of Almeydas, which includes the municipalities Villapinzón, Chocontá, Suesca, Sesquilé and Guatavita, (Ministerio de Ambiente y Desarrollo Sostenible, s.f.). The main characteristic of the area is the industrial activity due to the presence of tanneries. In figure 2 you can see the point where the water sampling was carried out.

Figure 2: Water sample collection site.

3. Methodology

This research was developed in two phases. In the first, 4088 g of the sample from the stem of a *Ulex Europaeus* dry shrub to the touch were collected in the study area. The stem was chosen because it facilitates the dry, polish and sift and it is the part of the plant that contains the least moisture (Milquez, 2017) and a high percentage of lignin, those are relevant for a higher yield in obtaining biochar because thermal conversion technologies like slow pyrolysis require raw material with a moisture content of less than 50% and the lignin has a great thermal stability (Urien, 2013). The drying process was carried out in the open air for 30 days, followed by polishing machine. Then the size of the stem was reduced, and the screening was carried out with a digital # 60 sieve (250 µm). Finally, it was placed in the oven at 105° C for 24 h and its moisture content was verified gravimetrically.

Slow pyrolysis was carried out at 450° C, 550° C and 650° C, in a Thermolyne Furnace 6000 muffle with a heating rate of approximately 8° C/min. Three individual samples of 90 mg of the *Ulex Europaeus* were processed at each temperature to obtain the produced biochar. A $NaHCO_3$ and $C_6H_8O_7$ pellet (Alka-Seltzer) was introduced into the muffle to displace the oxygen present in the muffle. Finally, some characteristics of the biochar produced were determined, such as the surface area found with the equation suggested in literature (Mc Cabe 2002), texture by touch method, yield percentage by difference in weights, and moisture content by gravimetric method. These parameters are the most important characteristics to consider for its use as an agent to remove contaminants from water (Kishimoto and Sugiura, 1985; Urien, 2013).

In the second phase, 3 L of water was collected from the Upper Bogotá River Basin and preserved with 1 mL/L of HNO_3 which lowered the pH to < 2. These sample was stored at 10° C during transportation. This sample was filtered by vacuum filtration to avoid interference from particles. The initial chromium concentration was determined by the Hach method 8024 with reading on a HACH DR2800 spectrophotometer. For the sorption experiments, 200 mL of the water sample was placed in contact for two hours with 20 mg of the biochar. This same procedure was carried out with 20 mg of powdered activated carbon, which served as a control for comparison. Finally, the adsorbent medium that presented the highest percentage of removal of chromium from the water was determined by measuring the concentration of chromium as described above.

4. Results and Discussion

4.1 Characteristics of the biochar obtained from the slow pyrolysis of *Ulex Europaeus.*

In total, 2,675 g of processed Ulex Europaeus material was obtained, corresponding to 65% of the sample taken from the bush, which offers a feasible alternative that allows reducing the volume of residue derived from eradication tasks. The measured moisture content was 33.2 % wt., a value that is within the recommended range for thermal conversion processes such as slow pyrolysis (Urien, 2013).

In the slow pyrolysis process, from each 90 g sample between 2 g and 18 g of biochar were obtained, with a surface area in all cases of 13.43 m2/g and a fine texture. These results are consistent because the biochar comes from the same sample and subjected to the same polishing and screening process. The value of the surface area obtained is within range consistent with activated carbon produced from pressed safflower seed paste (3.64-14.14 m2/g) (Angin et al, 2013). The texture is related to the surface area, since smaller particles have a greater specific surface area and therefore will have greater removal of chromium from the water. (Méndez, 2012, p.24). The yield percentage of each biochar obtained with respect to 65% of the sample taken from the bush is presented in Table 1.

Table 1: Biochar yield percentage

Temperature (°C)	Run	Initial weight (g)	Capsule weight (g)	Final weight (g)	Percentage yield (% wt.)
	1	256.46	166.46	182.46	6.24
450	2	265,00	175.00	195.73	7.82
	3	256.48	166.48	179.63	5.13
	1	256.45	166.45	170.50	1.58
550	2	252.77	162.77	167.94	2.05
	3	264.22	174.22	176.37	0.81
	1	252.76	162.76	171.45	3.44
650	2	256.55	166.55	184.84	7.13
	3	256.44	166.44	173.10	2.59

According to Urien 2013, the optimal biochar should yield between 25% to 35%; however, it is observed that the samples obtained a yield percentage lower than 8% (Table 1).

The composition, the humidity of the sample and the technology used for the pyrolysis process have an effect on the yield percentage. Following theoretical data, the percentage composition of the lignin in stem should be between 10-30 %, and moisture percentage should be less than 50% (Urien, 2013). Taking into account statements contained in the literature, using a high-efficiency technology for the pyrolysis process makes it possible to achieve mass yields of around 30-40% on a wet basis. (Escalante, 2016 cited in McHenry, 2009)

Even considering that the lignin percentage of the prickly broom is between a 11-15%, and the moisture of the sample was 33.2 % wt., the yields obtained are lower than optimal. Therefore, it can be said that the composition and the moisture of the spiny broom is not significantly influencing the yield percentage. However, in this case the muffle available for the pyrolysis process did not have the function of programming the heating rate, nor did it have a system with valves that allowed oxygen to be displaced for what was used a more rudimentary method to displace the oxygen, such as placing the Alka-Seltzer pellet in the muffle, could decrease the efficiency of the pyrolysis process and affect the yield in obtaining biochar.

4.2 Chromium removal

Table 2 indicates the results obtained from the removal of chromium from the water sample of the Bogotá River, when exposed for a contact time of 2 hours to the biochar obtained at 450° C, 550° C, and 650° C as well as the powdered activated carbon, this time was established following theoretical data of contact times for heavy metals removal from water with activated carbon that are in a range between 2 to 4 hours, according to kinetic test carried out by Sun-Kou and et al, 2014.

The initial concentration of chromium in water sample related to the activities of the tannery sector in Villapinzón (Villapinzón Municipal Mayor's Office, 2000) is similar to those reported by Castro & Molina, 2019. The concentration of 0.08 mg/L is above the permissible value of 0.05 mg/L stipulated in the Quality Objectives of the Bogotá River for the year 2020 consigned in Agreement 43 of October 17, 2006. Thus, this water is not safe for domestic and agricultural use and may be harmful to the flora and fauna (Castro & Molina, 2019).

Table 2: Final concentration of the water sample with biochar.

Temperature °C	Run	Initial concentration of Cr (mg/L)	Final concentration of Cr (mg/L)	Removal percentage (%)	Average removal percentage
	1	0.08	0.07	12.5	20.83
450	2	0.08	0.06	25	
	3	0.08	0.06	25	
	1	0.08	0.07	12.5	29.16
550	2	0.08	0.05	37.5	
	3	0.08	0.05	37.5	
	1	0.08	0.05	37.5	29.16
650	2	0.08	0.07	12.5	
	3	0.08	0.05	37.5	
Powdered activated-carbon.		0.08	0.07	12.5	12.5

The final concentration of chromium in the water sample indicates that the biochar that presented the highest percentage of removal were those obtained at temperatures of 550° C and 650° C. At temperatures higher than 500° C, biochar is more effective for removing pollutants from the water due to the more developed pore structures that have greater surface area for the attachment of the pollutant (Das et al., 2015). In two of its three replicates, the biochar produced at 550 ° C removed 37.5% of the chromium. This removal efficiency is greater than that reported by Parra et al (2018) in the removal of chromium from the biochar produced from *Boehmeria nivea* (22.8%). Activated carbon had a removal percentage below the three replicates of biochar obtained at 550° C and 650° C.

5. Conclusions

The pyrolysis of *Ulex Europaeus* this is an alternative that allows reduce the volume of vegetable waste destined for incineration, in a radio of 1:45 to 1:5, based on the percentage of biochar yield with respect to the thorny broom sample. The biochar obtained at 550° C and 650° C had chromium removal efficiency up to

37.5%. This finding corroborates the statement that at temperatures greater than 500° C, high porosity biochar is obtained, which favors the removal of chromium in the water. In relation to the traditional use of powdered activated carbon in the removal of pollutants, the use of biochar from the slow pyrolysis of *Ulex Europaeus* presents greater removal efficiency, positioning this product as an option to consider for the solution addressing problems in the mountain ecosystems of Colombia.
The yield of biochar production is directly proportional to the lignin composition of the sample, and its content must be greater than 10% so that the pyrolysis process achieves optimal use of energy capacity.

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